

CO-PROCESSING OF AGRICULTURAL AND BIOMASS WASTE WITH COAL

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INTRODUCTION

A major thrust of our research program is the use of waste materials as co-liquefaction agents for the first-stage conversion of coal to liquid fuels. By fulfilling one or more of the roles of an expensive solvent in the direct coal liquefaction (DCL) process, the waste material is disposed off ex-landfill, and may improve the overall economics of DCL. Work in our group has concentrated on co-liquefaction with waste rubber tires, some results from which are presented elsewhere in these Preprints. In this paper, we report on preliminary results with agricultural and biomass-type waste as co-liquefaction agents.

The ideal co-liquefaction agent has, at a minimum, three characteristics: it should be available in an unlimited supply; it should be expensive to dispose of, whether in a landfill or by other means; and it should contain components which can function as hydrogen-transfer agents and/or termination agents for free radicals. The first two of these allow for a significant economic impact on the DCL process, and the last ensures good processing properties. While no single agent fulfills all these requirements, the two categories used in the present work are viable candidates. In the category of biomass-type waste, we have used sawdust. In the category of agricultural waste, we have used horse manure, cow manure, and a more-prosaic (but perhaps more-reproducible) commercially available manure ("Supermanure").

All of these agents contain varying amounts of the following components: extractables (oils), cellulose, hemi-cellulose, lignin and ash. Typically, extractables can be removed by a simple water extraction. The insolubles, when extracted with concentrated HCl, yield a soluble cellulose/hemicellulose portion. The HCl-insoluble when subjected to NaOH extraction, yield lignin as the soluble phase while ash is classified as NaOH- (and HCl-) insoluble. Cellulose and hemi-cellulose have a more-or-less well defined structure, with six-membered rings of $-C_6H_5O(OH)_2CH_2OH$ linked with $-O-$. The structure of lignin is much less defined, but is known to contain building blocks of phenylpropane with α -alkyl ether linkages and/or β -4' ether linkages. Breakage of these linkages may well involve DCL-solvent-like properties.

EXPERIMENTAL

Standard tubing-bomb reactors were used. They were filled with either coal alone or equal weights of coal and one of the co-liquefaction agents described above. The coal used throughout these runs was a high-volatile-A bituminous coal from the Blind Canyon seam, Utah, coded as DECS-6 by the Pennsylvania State University Coal Bank. The coal was ground to -60 mesh under nitrogen. For consistency with previous work, a small amount of sulfiding agent (0.1 ml CS_2) was added to all run batches. Reactions were carried out both in the absence of any additional solvent and with 5 ml of tetralin. Standard reaction conditions were used: 1000 psi (cold) hydrogen, 350°C, vertical agitation at 500 cpm, 1 h. After the reaction, the total conversion (of all solids) and the yields of asphaltene and preasphatene and oil+gas were obtained by solution of the remaining solids in tetrahydrofuran and n-hexane. Additional details can be found in e.g. [1]. Runs were repeated at least once. The reproducibility is typically 2%.

RESULTS AND DISCUSSION

Results for the co-liquefaction of DECS-6 coal and sawdust are summarized in Table I. Liquefaction results of the sawdust alone are significantly greater than those of the coal alone. The addition of tetralin improves the coal-alone results considerably, especially the yield of asphaltene+preasphaltene. The "DIFFERENCE" entries refer to the improvement (if positive) in the results of coal plus sawdust runs, relative to the average of the individual coal and sawdust runs. In the absence of tetralin, there is an improvement in the oil+gas yield at the expense of the asphaltene+preasphaltene yield, while the improvement in the total conversion is within experimental limits. These results indicate that sawdust may catalyze the formation of asphaltenes to oils or may cap low-molecular-weight radicals or other species to prevent retrograde formation of asphaltenic products by combination of oil-range products. The former appears to be unlikely in the light of the results with tetralin: in conversion and yields, there is negligible difference between the individual coal and sawdust runs and the coal-plus-sawdust run. Clearly, the sawdust under liquefaction conditions acts more as a solvent than a catalyst; when tetralin, a powerful solvent, is present, its effect overwhelms that of sawdust. Finally, it is interesting to note that the oil+gas yield after the run with sawdust plus coal is undistinguishable from that when tetralin is also added. Hence, the effects of 5 ml tetralin can be suitably substituted for by 3 g of sawdust. This is obviously of great economic importance.

Results with "Supermanure" are shown in Table II. As in Table I, the co-liquefaction agent alone shows greater conversion and oil+gas yield than coal alone, and the addition of the tetralin has a much smaller effect on the co-liquefaction agent alone than on the coal alone. In the absence of tetralin, the addition of "Supermanure" to the coal increases the oil+gas yield but decreases the overall conversion. Both changes are slight, but significant. In the presence of tetralin, the addition of "Supermanure" to coal appears to decrease the oil+gas yield fairly substantially and also decreases the total conversion slightly. This is a different effect than that observed in Table I. Clearly the constituents of sawdust and "Supermanure" are different, and this is manifested in the behavior when tetralin is present.

Table III summarizes the behavior of cow manure as a co-liquefaction agent. Acting alone, this agent is not liquefied as readily as "Supermanure" and does not yield as much oil+gas fraction. However, in the presence of coal, with or without tetralin present, there is a significant difference (improvement) in oil+gas yield, and this is achieved at the expense of the asphaltenic fraction.

Finally, we indicate in Table IV the effect of horse manure as a co-liquefaction agent. In the absence of tetralin, the presence of horse manure significantly improves the total conversion, and that difference is manifested almost entirely in the oil+gas yield. In the presence of tetralin, the difference in total conversion after adding horse manure is even larger, but that difference is manifested to a large extent in improving the asphaltenic yield. The total conversion and the yield of asphaltenic+preasphaltenic fractions are significantly increased when tetralin is added; the oil+gas yield is also increased but to a lesser extent. Clearly the effect of horse manure is not just to act as a substitute for a more-expensive solvent; there may well be some catalytic effects involved.

The temptation to ascribe the differences in behavior of manure from the horse and cow to differences in the diet of these two species is strong. However, we have not yet carried out analyses of these two co-liquefaction agents to test our hypothesis.

CONCLUSIONS

In the absence of tetralin, the total conversion of equal parts of

coal and a co-liquefaction agent is approximately equal for sawdust, "Supermanure" and horse manure; the value for cow manure is somewhat smaller. However, the greatest improvement (over the conversion of individual reactants) occurs for horse manure; the conversion for "Supermanure" is significantly smaller than the sum of the individual values. The absolute values of the oil+gas yields follow the same trends as those observed for the total conversions; and the improvement of this yield (over yields of individual reactants) also follows the same trends as the improvement of the total conversions.

In the presence of tetralin, both the absolute value of the total conversion and the improvement over conversions of individual species are observed for horse manure as the co-liquefaction agent. The total conversion is almost doubled when tetralin is present, relative to the value in the absence of tetralin, the absolute values of the oil+gas yield are somewhat greater for horse manure and for sawdust than for the other two. Interestingly, the greatest difference, i.e., improvement over individual oil+gas yields, is observed for the case of cow manure as the co-liquefaction agent. In fact, all other improvements in oil+gas yields are either negligible or negative.

Hence the use of biomass-type and agricultural waste as agents of co-liquefaction of coal is in general worthy of consideration.

REFERENCES

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TABLE I
Results for Sawdust/Coal Co-Liquefaction

Sawdust	Coal	Tetralin	Total Conversion (%)	Asphaltene+Preasphaltene Yield (%)	Oil+Gas Yield(%)
No	Yes	No	22.4	17.3	5.1
Yes	No	No	70.4	7.7	62.7
Yes	Yes	No	47.6	8.7	38.9
(DIFFERENCE)		No	+1.2	-3.8	+5.0
No	Yes	Yes	57.0	50.0	7.0
Yes	No	Yes	93.1	28.5	64.5
Yes	Yes	Yes	74.7	38.2	36.5
(DIFFERENCE)		Yes	-0.3	-0.8	+0.5

TABLE II
Results for "Supermanure"/Coal Co-Liquefaction

Supermanure	Coal	Tetralin	Total Conversion (%)	Asphaltene+Preasphaltene Yield (%)	Oil+Gas Yield(%)
No	Yes	No	22.4	17.3	5.1
Yes	No	No	80.0	18.0	62.0
Yes	Yes	No	48.2	11.9	36.3
(DIFFERENCE)		No	-3.0	-5.8	+2.7
No	Yes	Yes	57.0	50.0	7.0
Yes	No	Yes	87.4	23.5	63.9
Yes	Yes	Yes	69.6	38.4	31.2
(DIFFERENCE)		Yes	-2.6	+1.6	-4.3

TABLE III
Results for Cow-Manure/Coal Co-liquefaction

Cow Manure	Coal Tetralin	Total Conversion (%)	Asphaltene+Preasphaltene Yield (%)	Oil+Gas Yield(%)
No	Yes	22.4	17.3	5.1
Yes	No	57.4	17.8	39.6
Yes	Yes	39.8	12.2	27.6
(DIFFERENCE)	No	-0.1	-5.4	+5.2
No	Yes	57.0	50.0	7.0
Yes	Yes	66.9	17.7	49.2
Yes	Yes	62.1	29.2	32.9
(DIFFERENCE)	Yes	-0.1	-4.7	+4.8

TABLE IV
Results for Horse-Manure/Coal Co-liquefaction

Horse Manure	Coal Tetralin	Total Conversion (%)	Asphaltene+Preasphaltene Yield (%)	Oil+Gas Yield(%)
No	Yes	22.4	17.3	5.1
Yes	No	66.2	13.4	52.8
Yes	Yes	48.2	14.4	33.8
(DIFFERENCE)	No	+3.9	-1.0	+4.8
No	Yes	57.0	50.0	7.0
Yes	Yes	88.2	22.1	66.1
Yes	Yes	81.5	43.4	38.1
(DIFFERENCE)	Yes	+8.9	+7.3	+1.5